

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 August 2002 (01.08.2002)

PCT

(10) International Publication Number
WO 02/059201 A1

(51) International Patent Classification⁷: **C08L 67/02.**
67/04

(21) International Application Number: PCT/EP02/00761

(22) International Filing Date: 25 January 2002 (25.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
TO2001A000061 25 January 2001 (25.01.2001) IT

(71) Applicant (for all designated States except US): **NOVA-MONT S.P.A.** [IT/IT]; Via G. Fauser, 8, I-28100 Novara (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BASTIOLI, Ca-**
tia [IT/IT]; Via Della Noce, 16, I-28100 Novara (IT). **DEL TREDICI, Gianfranco** [IT/IT]; Via Sempione,
31, I-21018 Sesto Calende (IT). **GUANELLA, Italo**
[IT/IT]; Via Sant'Ambrogio, 54, I-28068 Romentino (IT). **FLORIDI, Giovanni** [IT/IT]; Via XIII Martiri 8, I-28100
Novara (IT). **PONTI, Roberto** [IT/IT]; Via Momo, 64,
I-28047 Oleggio (IT).

(74) Agents: **RAMBELLI, Paolo** et al.; Jacobacci & Partners
S.p.A., Corso Regio Parco, 27, I-10152 Torino (IT).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

IK, IR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW).
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM).
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR). OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted
a patent (Rule 4.17(ii)) for the following designations AE,
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA,
CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES,
FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG,
MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU,
SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG,
UZ, VN, YU, ZA, ZM, ZW; ARIPO patent (GH, GM, KE, LS,
MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent
(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent
(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,
MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI,
CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/059201 A1

(54) Title: BINARY MIXTURES OF BIODEGRADABLE ALIPHATIC POLYESTERS AND PRODUCTS OBTAINED FROM THESE

(57) Abstract: A biodegradable mixture obtained by melt mixing polyesters comprising: (A) an aliphatic polyesters of the kind polyhydroxyacid or diacid/diol and their copolymer; (B) a polymer of lactic acid comprising L or D polylactic acid, L, D-polylactic, meso polylactic acid and lactic acid copolymers with hydroxyacids or lactones thereof containing at least 75% of L-lactic or D-lactic acid in which the concentration by weight of A with respect to (A+B) is in the range 30-60% and in which the sum of the fusion enthalpies ΔH_A and ΔH_B of the two polyesters in the mixture is greater than the normalized sum of the fusion enthalpies Δ_1 and Δ_{H2} of the aliphatic polyesters prior to melt mixing, the fusion enthalpy converted to the polylactic acid-family polymer when the temperature of the film is raised being greater than 35 J/g.

Binary mixtures of biodegradable aliphatic polyesters and products obtained from these

The present invention relates to biodegradable mixtures comprising at least two aliphatic polyesters in proportions such that it is possible to obtain a film, by blowing or casting, provided with improved water barrier properties with respect to individual polyesters, of high rigidity, transparency and biodegradability as well as solid and expanded (foamed) sheets and associated thermoformed products with optimum barrier properties and rigidity.

Such composite materials are particularly suitable for the food packaging sector for rigid films which easily form a skin, expanded and solid containers, dishes and casting etc.

Prior Art

Conventional polymers such as polystyrene, polyethylene terephthalate and similar are characterised not only by an excellent rigidity, but also by good barrier properties against water and by good transparency. These polymers are used in the packaging sector in general, and in food packaging in particular, as well as in the sector of disposable dishes such as plates, cups and cutlery. Their low biodegradability and the difficulty of recovering the different starting plastics in a sufficiently differentiated manner upon recycling has however created an increasing problem of disposal in recent decades.

Polymers such as L-poly-lactic acids, D,L-poly-lactic acids, D-poly-lactic acids and their co-polymers are biodegradable thermoplastic materials from renewable sources; they are

transparent with excellent resistance to fungi and therefore suitable for packaging food as well as preservation of their organoleptic characteristics. On the other hand they biodegrade slowly in the soil and, in compost, degrade quickly only at high temperatures. The greatest limitation, however, lies in the low processability, upon recycling of waste, and also in that for many applications the permeability to water is too high. In food packaging there is moreover a not insignificant difficulty of welding.

If, on the other hand, aliphatic polyesters constituted predominantly of monomers from renewable sources starting from diacidic diols are considered, these have the limitation that their rigidity is too low and their water permeability is too high. For this reason products prepared from these resins are also inadequate as rigid materials for packaging.

Binary mixtures of polylactic acid and aliphatic polyesters have constituted the subject of many patents. In particular, European Patent EP-0 980 894 A1 (Mitsui Chemical) claims a significant improvement in the tear strength and balance of film based on a blend of polylactic acid and other polyesters such as polybutylene succinate, with a melting point of between 80 and 250° C, by introducing a plasticiser into the blend. This, however, gives a non-transparent film with, in any event, very modest strength of the order of 120g in accordance with the JIS P8116 method. The presence of a plasticiser, moreover, places limitations on contact with food, and the disadvantage of ageing phenomena.

US Patent US 5,883,199 relates to binary mixtures of polylactic acid and polyester with the polyester forming a continuous or co-continuous phase and the polylactic acid

content lying between 10 and 90%. Such mixtures, in accordance with the indicated examples, do not show significant reduction in the permeability to water or steam.

EP-1 033 383 relates to a biodegradable film comprising a polylactic acid-family polymer and other aliphatic polyester than the polylactic acid-family polymer characterized in that the heat for fusion converted to the polylactic acid-family polymer when the temperature of the film is raised is 35 J/g or under. Such patent does not deal with the problem of improving the barrier properties against water of the biodegradable film.

Subject of the invention

Starting from the problem of finding a material able to combine properties of transparency, rigidity and water barrier it has now surprisingly been found that by combining a polymer of polylactic acid with aliphatic polyesters of the kind polyhydroxyacid or diacid/diol or their copolymers in specific ratios as described hereinafter there is a critical range of compositions in which it is possible to obtain, entirely unexpectedly, a significantly lower permeability to water with respect to the individual polymers, as well as modulus of elasticity in tension greater than any envisaged from the Halpin/Tsai mixture rule, and an optimum transparency.

Description of the invention

The invention relates to a biodegradable mixture obtained by melt mixing polyesters comprising:

(A) An aliphatic polyester of the kind polyhydroxyacid, with the exclusion of polymers of lactic acid, or diacid/diol or their copolymers with modulus of elasticity lying between 400 and 900 MPa and breaking elongation greater than 200%, more preferably greater than 300%, on blown film of about 25-30 μm , average ponderal molecular weight greater than 55,000 and more preferably greater than 65,000, and melting point lying between 40 and 95° C; preferably between 55 and 85° C and more preferably between 57 and 79° C;

(B) A polymer of lactic acid comprising L or D polylactic acid, L,D-polylactic, meso polylactic acid and lactic acid copolymers with hydroxyacids or lactones thereof containing at least 75% of L-lactic or D-lactic acid with average ponderal molecular weight higher than 70,000 and with a modulus of elasticity greater than 1500 MPa;

in which the concentration by weight of A with respect to (A+B) is in the range 30-60% and in which blown film of a thickness of 25 - 30 μm has modulus of elasticity greater than 1400MPa, permeability to water comprised from 170 to 40 g30 $\mu\text{m}/\text{m}^2\text{24h}$, a transmittance measured at the entrance port lying between 90 and 95% and in which the sum of the fusion enthalpies ΔH_A and ΔH_B of the two polyesters in the mixture is greater than the normalized sum of the fusion enthalpies ΔH_1 and ΔH_2 of the aliphatic polyesters prior to melt mixing, the fusion entalpy converted to the polylactic acid polymer being greater than 35 J/g .

For normalised sum it is meant the sum obtained by multiplying the ΔH_1 and ΔH_2 fusion entalpies for the

percentage divided by 100 of the two polyesters present in the mixture.

The increase of the fusion enthalpies $\Delta H_A + \Delta H_B$ of the two polyesters in the mixture with respect to their normalised sum $\Delta H_1 + \Delta H_2$ shows an unexpected increase of cristallinity in the mixture which is the cause of the surprisingly very low value of the permeability to water exhibited by the composition according to the invention.

The mixture of biodegradable polyesters according to the invention is obtained from a process which involves working in a twin screw or single screw extruder in temperature conditions between 140 and 200° C, performing the two steps of the mixing process and film forming together or separately. Film forming separate from the mixing process is achieved with conventional machines for the extrusion of low or high density polyethylene with a temperature profile in the range between 100 and 200° C, and it is possible to obtain films having thicknesses lying between 5 and 250 μm . Film forming at temperatures lying between 150 and 200° C is preferred.

Film with thicknesses of 25-30 μm has characteristics of transparency lying in the range 35-80% for the source transmittance, and in the interval 90-95% for the entry point transmittance. The permeability to steam or water at 38° C with a relative humidity on one side of the film of 10%, to obtain a Δ relative humidity of 90% in static conditions, lies between 170 and 40 grams of water referred to 30 μm of thickness of the film which passes through a square metre of surface in twenty-four hours ($\text{g}30\mu\text{m}/\text{m}^224\text{h}$) and more

preferable between 120 and 70 grams ($g30\mu m/m^224h$). The individual polymers constituting the mixture according to the invention, in the same film conditions, give values of permeability lying between 200 and 800 gr. ($g30\mu m/m^224h$).

The tensile properties in the longitudinal film direction in terms of modulus of elasticity measured according to ASTM 882 exceed 1000 MPa and preferably 1400 MPa.

In the mixing phase polymers of type A with MFI ($150^\circ C$, 2.16 kg) lying between 1 and 10 dg/min are preferred and polymers C with MFI ($190^\circ C$, 2.16 kg) lying between 2 and 30 dg/min are preferred.

As above specified, polymer (A) includes polyhydroxyacids, with the exclusion of polymers of lactic acid, and/or dicarboxylic aliphatic acids/ aliphatic diols polyesters and their copolymers.

Typical monomers of the polyhydroxyacids include glycolic acid, 3-hydroxybutyric, 4-hydroxybutyric, 3-hydroxyvaleric, 4-hydroxyvaleric, and 6-hydroxycaproic acid and further includes cyclic esters of hydroxycarboxylic acids such as glycolides, dimers of glycolic acid, ϵ -caprolactone and 6-hydroxycaproic acids. Preferred monomer is ϵ -caprolactone. Mixtures of these acids can be used. These acids are also suitable as comonomers for the diacid/diol polyesters.

Examples of diacids are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassylic acid, undecandioic acid, and dodecandioic acid. Azelaic acid, sebacic acid and brassylic acid are preferred.

Specific glycols are ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, 1,2- and 1,3-propylene glycol, 1,3-butandiol, 1,4-butandiol, 3-methyl - 1,5-pentandiol, 1,6-hexandiol, 1,9-nonandiol, dipropylene glycol, 1,11-undecandiol, 1,13-tridecandiol, neopentyl glycol, polytetramethylene glycol, 1,4-cyclohexane dimethanol and cyclohexane diol. Mixtures of these compounds can be used.

All the compounds discussed above are combined in such a way as to form polyesters with mechanical characteristics of tensile resistance to elongation greater than 300% and modulus of elasticity lying between 400 and 900 MPa on blown films of at least 30 μm thickness and with a melting point between 40 and 95° C, preferably between 55 and 85° C and more preferably between 57 and 79° C. Particularly preferred polyesters are poly- ϵ -caprolactone and its copolyesters.

Also included in polymers of type A are polyamide polyesters where the polyester part is as described above and the polyamide part can be caprolactam, and aliphatic diamine such as hexamethylene diamine or even an amino acid. The type A polyesters can also contain aromatic diacids in quantities less than 5 moles%. Polycarbonates also belong to polymers of type A.

The polyesters can be polymerised via polycondensation or, as in the case of glycolides and lactones, by ring opening as known in the literature. Moreover, polyesters can be branched polymers with the introduction of polyfunctional monomers such as glycerine, epoxyoized soya oil, trimethylpropane and

the like or polycarboxylic acids such as butantetracarboxylic acid.

Regrading with isocyanates can take place in the molten state at the end of the polymerisation reaction or in the extrusion phase, or in the solid state as described in the Novamont Patent WO 99/28367. The two types of polymers A and B can also have additives such as chain extenders or cross linking agents of the type described above in the mixing phase.

Ratios between polymer A and polymer B different from those described for the mixtures according to the present invention give rise to products not having sufficient barrier properties and, in the case of excessively high content of polymer A, excessively low modulus of elasticity.

The material obtained from the mixture of two polymers A and B has no need for plasticisers which create problems of migration especially for food packaging. However, quantities of plasticisers below 5% with respect to polymers A + B can be added.

Various additives can also be incorporated in the mixture, such as antioxidants, UV stabilisers, stabilisers against heat and hydrolysis, flame retardants, slow release agents, organic and inorganic fillers such as, for example, natural fibres, anti-static agents, humectants, colorants and lubricants.

In particular, in the production of blown or cast film the following can be added: silica, calcium carbonate, talc, kaolin, kaolinite, zinc oxide, wollastonites, various hydrotalcites and in general lamellar inorganic substances

whether or not functionalised with organic molecules capable of delamellating in the mixing phase with the polymeric mixture or with one of the individual polymers of the mixture to give nanocomposites with improved antiblocking and barrier properties. The various inorganic substances can be used in mixtures or with individual products. The concentration of the inorganic additives is generally between 0.05 and 30%, preferably between 0.5 and 20%.

To improve the film-forming characteristics there can be added amides of aliphatic acids such as oleamide, stearamide, erucamide, behenamide, N-oleylpalmitamide, N-stearyl erucamide and other amides, salts of fatty acids such as aluminium, zinc or calcium stearate and the like. The quantities of these additives vary from 0.05 to 7 parts and preferably between 0.1 and 5 parts of the polymer mixture.

The mixture thus obtained can be transformed into a film by blowing or extrusion through a flat head, can be extruded as a solid sheet or a foamed or expanded sheet and then heat formed. The films are transparent, have a high resistance to water (water barrier) with respect to the biodegradable starting materials according to CEN 13432, and moreover have a sufficient rigidity for food packagings which require rigid films. The film is weldable and can be obtained in thickness up to 5 μ m by blowing or casting.

In the non-food field the films obtained with the mixture according to the invention are excellent for applications such as films for adhesive tape, tapes for nappies, for ornamental coloured tapes, for adhesive tapes of different form and use and moreover in applications such as bags for

clothing, or film for wrapping flowers, plants and gift objects.

In the food field the films obtained with the mixture according to the invention are excellent for applications such as packets for dried products (biscuits, crackers, crisps, chipsters and the like), chocolate, cheese, meat, vegetables etc. and in applications such as joining and tear strip films for sealing containers.

The films advantageously find use also in agriculture or in any event for outside use and can contain UV stabilisers in the form of individual films or coextrusions with films having a low modulus, as in the case of starch-based materials, to give improved UV resistance, improved barrier properties, and a different rate of degradation in the atmosphere and in the soil.

The films can moreover be surface treated with aluminium or silica or others, and can be laminated with other materials so as to combine different characteristics (barrier to oxygen and/or to water, peelability, connectability etc). For these cases, as particularly advantageous examples of practical applications, one can mention containers for yoghurt, cheese, meat, bread, biscuits, potatoes and snacks in general, bowls for industrial use, and containers for fragile objects such as eggs.

The films can advantageously be used as the weldable component of a multi-layer film composed of at least one layer of polylactic acid or other polyester, non-structured starch (and its blends with synthetic and natural polymers) or as components of a multi-layer with aluminium and other

materials or with a vacuum metalised layer with aluminium, silica and other inorganic materials. The multi-layers can be obtained by coextrusion or by lamination or by extrusion coating, if one layer is paper or other material which does not melt between 100 and 200° C.

The biodegradable polymer mixtures according to the invention can moreover find advantageous use in the form of products obtained using other techniques than film forming. For example, they can be used to obtain fibres for textiles and non-woven textiles, or for fishing nets. Moreover, the non-woven fabric can be used in the sanitary sector for nappies, sanitary towels etc. The fibres can also be utilised as weldable reinforcing fibres in special papers.

The material can also be utilised with success also for the production of sheets for thermoforming, extruded or coextruded with other layers of polymers such as polylactic acid or other polyesters or polyamides or materials based on starch then thermoformed to form containers for food, agriculture and others. The material can be used for injection moulding of containers, cutlery or other things, and has a very high speed of crystallisation and a very high crystallinity.

The material can also have polymeric additives such as polyethylene waxes and polypropylene, PET and PTB, polystyrene, copolymers of ethylene and propylene with functional carboxylic groups, carboxylate, methacrylate, acrylate or hydroxylic groups or else combined with these polymers in coextrusions, coinjections or the like. The material can be utilised as a matrix in the blend with destructured starch according to the processes described in

Novamont Patents (EP-0 327 505, EP-0 539 541, EP-0 400 532, EP-0 413 798, EP-0 965 615) with the possibility of forming complexes with the starch or simply utilising the destructured starch, converted and/or complexed as a submicronic filler for the polyester.

They can be used as coating films for biodegradable expanded materials based on polyesters, polyamides, thermoplastic starch and complexed starch or simply blends of starch with other polymers or with the material of the present invention.

The material, on its own or in mixture with starch or other polymers can be obtained as an expanded material to form containers for fruit and vegetables, meat, cheese and other food products, or containers for fast food. It can also be obtained in the form of expanded particles which can be agglomerated for industrial packaging or in the form of injected foam.

The mixture according to the invention will now be described with the following non-limitative examples.

Examples

Example 1

Polymers constituting the mixture:

- Aliphatic polyester: poly- ϵ -caprolactone (TONE 787 Union Carbide)
- Poly L-lactic acid with a D-lactic content of 6%: 4040 Cargill.

Formed into a film on a Ghioldi machine:

Diameter = 40mm, L/D = 30; rpm=45; die: diameter = 100mm; air gap = 0.9mm; land = 12; flowrate = 17 kg/h; temperature

profile: 120-150-190x2; temperature filter = 190x2; head temperature = 190x2.

Film: width = 400mm; thickness = 25 μ m.

The determination of the values of transmittance, both at the source port (T_{SOURCE}) and at the entry port (T_{entr}) was effected by means of a HAZEGUARD SYSTEM XL-211.

The values of breaking load (α), elongation at break (ϵ) and modulus of elasticity (E) were determined in accordance with the ASTM D 882-91 by means of an INSTRON 4502 instrument.

The values of permeability, expressed in g30 μ m/m²24h were determined at 38° C with a relative humidity of 10% on one side of the film to guarantee a Δ humidity equal to 90% in static conditions with cups of diameter 61.8mm and a depth of 28.5mm filled with H₂O to a height of 10mm from the bottom. The cups were put in a climatic cell positioned within a perforated box which guarantees the absence of air currents within it which may cause possible turbulence phenomena on the surface of the specimen, and thus an uncontrolled increase in the exchange efficiency. The values found identify the grams of water referred to 30 μ m of thickness of film which passed through a square metre of surface in twenty-four hours.

Comparative examples 2-6

Examples 2 and 2a refer to the pure polylactic acid respectively with and without 0,3% erucamid (slipping agent).

Examples 3-6 were made with BIONOLLE a commercially available aliphatic polyester: examples 3-4 with BIONOLLE 1903 (polybutylensuccinate homopolymer) and example 5-6 with

Bionolle 3001 (polybutylensuccinate-adipate copolymer). These examples show permeability values outside the range of the compositions according to the present invention.

Results of the tests conducted are plotted in Table 1.

Table 2 shows the ΔH values referred to the polyesters prior to melt mixing (ΔH_1 and ΔH_2) and to the polyesters in the mixture (ΔH_A and ΔH_B). The table refers to the compositions of examples 1, 4 and 6. Example 1 is according to the invention whereas examples 4 and 6 refer respectively to Bionolle 1903 and Bionolle 3001.

The values have been determined on films of about 25-30 μm . A Perkin Elmer DSC 7 analyzer was used. ΔH_1 and ΔH_2 are the fusion entalpy values of the polyesters. $\Delta H_1 + \Delta H_2$ is the sum of the heat fusion values normalized in relation to the mixtures percentages. The values are expressed in J/g. The Differential Scanning Calorimetry has been performed raising the temperature at a ratio of 20°C per minute.

According to example 1 the fusion entalpy converted to the polylactic acid polymer is 39.8.

TABLE 1

Exam ple	A %	B %	A/A+B	Permeability g30 μ m/m ² 24h	T _{source} %	T _{entr} %	σ (MPa)	ϵ (%)	E (MPa)
1	50	50	50	50	66.9	93.7	32	72	1887
2	0	100	0	274	92	95	58	6	2517
2a	0	100	0	292	-	-	-	-	-
3	100	0	100	635	70.5	94.0	64	355	790
4	50	50	50	180	82	94.0	47	281	1580
5	100	0	100	1013	73	94.0	62	505	332
6	50	50	50	269	83	94.0	43	386	1327

TABLE 2

Exam ple	Polyester: Polylactic acid	Polye ster ΔH_1	Polylactic acid ΔH_2	$\Delta H_1 +$ ΔH_2	Polye ster ΔH_A	Polylactic acid ΔH_B	$\Delta H_A +$ ΔH_B
1	50:50	77.1	29.9	53.5	45	19.9	64.9
4	50:50	59	29.9	44.5	13.99	22.57	36.56
6	50:50	38	29.9	33.95	11.8	14.9	26.7

CLAIMS

1. A biodegradable mixture obtained by melt mixing polyesters comprising:

(A) An aliphatic polyester of the kind polyhydroxyacid, with the exclusion of polymers of lactic acid, or diacid/diol and their copolymers said polyester having modulus of elasticity comprised from 400 to 900 MPa and breaking elongation greater than 200% on blown film of about 25-30 μ m, average ponderal molecular weight greater than 55,000 and melting point from 40 to 95° C;

(B) A polymer of lactic acid comprising L or D polylactic acid, L,D-polylactic, meso polylactic acid and lactic acid copolymers with hydroxyacids or lactones thereof containing at least 75% of L-lactic or D-lactic acid with average ponderal molecular weight higher than 70,000 and with modulus of elasticity greater than 1500 MPa;

in which the concentration by weight of A with respect to (A+B) is in the range 30-60% and blown films of thicknesses of 25 - 30 μ m have modulus of elasticity greater than 1400 MPa, permeability to water comprised from 170 to 40 g30 μ m/m²24h and in which the sum of the fusion enthalpies ΔH_A and ΔH_B of the two polyesters in the mixture is greater than the normalized sum of the fusion enthalpies ΔH_1 and ΔH_2 of the aliphatic polyesters prior to melt mixing, the fusion enthalpy converted to the polylactic acid polymer being greater than 35 J/g.

2. A mixture according to Claim 1, in which the blown film obtained from mixtures of polymers (A) and (B) has and a transmittance at the entrance port lying between 90 and 95%.

3. A mixture according to the preceding claims in which the hydroxy acid monomer of the polyhydroxyacid comprises glycolic acid, 3-hydroxybutyric, 4-hydroxybutyric, 3-hydroxyvaleric, 4-hydroxyvaleric, 6-hydroxycaproic, and further includes cyclic esters of hydroxycarboxylic acids such as glycolides, dimers of glycolic acid, ϵ -caprolactone and 6-hydroxycaproic acid.

4. A mixture according to the preceding claims, in which the polyhydroxyacid is poly- ϵ -caprolactone or its copolymers.

5. A mixture according to Claims 1-2, in which the diacid in the diacid/diol polyester is sebacic acid, brassylic acid and azelaic acid or mixtures thereof.

6. A mixture according to Claim 5 in which the diol in the diacid/diol polyester is ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, 1-2 and 1-3 propylene glycol, 1, 3-butandiol, 1,4-butandiol, 3-methyl-1,5-pentandiol, 1,6-hexandiol, 1-9 nonandiol, dipropylene glycol, 1, 11-undecandiol, 1,13-tridecandiol, neopentyl glycol, polytetramethylene glycol and 1,4-cyclohexane dimethanol, cyclohexane diol or mixtures of these.

7. A mixture according to any preceding claim containing plasticisers in quantities less than 5% by weight with respect to the quantity of aliphatic polyester and polymer of the lactic acid.

8. A film produced by blowing or flat head extrusion with mixtures of biodegradable polymers according to any preceding claim.

9. A film according to Claim 8, in which the mixture comprises one or more inorganic additives such as silica, calcium carbonate, talc, kaolin, kaolinite, oxide of zinc, wollastonite, hydrotalcite, lamellar inorganic substances functionalised or not with organic molecules capable of delamellating in the mixing phase with the polymeric mixture or with one of the individual polymers of the mixture to give nanocomposites.
10. A film according to Claim 9, in which the concentration by weight of inorganic additives in the mixture lies between 0.05 and 30.
11. Packets for food or industrial products and clothing, adhesive tapes, tapes for nappies, coloured ornamental tapes, adhesive tapes of different form, film for packaging flowers, plants and gift items, produced from film according to any of Claims 8 to 10.
12. Bags and films for dry products such as bread, biscuits, crackers, crisps, chipsters, chocolate, cheese, meat, vegetables, welding and tear tape, and film for sealing containers, produced from film according to any of Claims 8 to 10.
13. Film according to any of Claims 8 to 10 surface treated with aluminium or silica or laminated.
14. Film according to any of Claims 8 to 10 as component of multi-layer film composed of at least one layer of polylactic acid or other polyester or destructured or non-destructured starch and its blends with synthetic and natural polymers or components of the multi-layer film with aluminium and other

materials or with a vacuum-metalised layer with aluminium, silica and other inorganic materials.

15. Fibres for woven and non-woven textiles or for fishing nets produced with mixtures according to any of Claims 1 to 7.

16. Sheets for thermoforming, extruded or coextruded with other layers of polymers then thermoformed into trays for food, agricultural products with biodegradable polymeric mixtures according to any of Claims 1 to 7.

17. Containers for yoghurt, cheese, meat, biscuits, crisps, snacks, trays for industrial use, containers for fragile objects, produced from sheet according to Claim 16.

18. Containers, cutlery, disposable objects, injection moulded from biodegradable polymeric mixtures according to any of Claims 1 to 7.

19. Foam sheet produced with biodegradable polymeric mixtures according to any of Claims 1 to 7 and formed into containers for food such as meat, cheese, vegetables, drinks, containers for fast food and for the industrial sector.

20. Agglomerable expanded particles produced from biodegradable polymeric mixtures according to Claims 1 to 7 for packages for use in the industrial sector.

21. Use of the biodegradable mixture according to any of claims 1 to 7 for applications requiring low water permeability values.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/00761

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L67/02 C08L67/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	POLYMER DEGRADATION AND STABILITY, vol. 59, 1998, pages 161-168, XP004294370 page 161, column 2, paragraph 2 page 162, column 1, paragraphs 1,2 table 3	1-5,8, 11,12
X	WO 94 07941 A (CARGILL INC) 14 April 1994 (1994-04-14) claim 10 claims 17,18 example 1; table 2	1-5,7-12
X	US 5 866 634 A (UEDA SHUHEI ET AL) 2 February 1999 (1999-02-02) claim 1 column 2, paragraphs 3,4 examples 5,6; table 1	1-5,8, 11,12

-/--

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

17 April 2002

Date of mailing of the international search report

29/04/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Lauteschlaeger, S

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/00761

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA 2 057 668 A (NOVACOR CHEM INT) 14 June 1993 (1993-06-14) claims 8,9 example 1 page 6, paragraphs 1,2 -page 7, paragraph 3 ---	1-3,19
Y	IANNACE S ET AL: "POLY(3-HYDROXYBUTYRATE)-CO-(3-HYDROXYVALE RATE)/POLY-L-LACTIDE BLENDS: THERMAL AND MECHANICAL PROPERTIES" JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY AND SONS INC. NEW YORK, US, vol. 54, no. 10, 5 December 1994 (1994-12-05), pages 1525-1535, XP000514124 ISSN: 0021-8995 page 1526, column 1, paragraph 4 table IV page 1527, column 2 ---	1-3,19
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 05, 30 April 1998 (1998-04-30) & JP 10 024518 A (MITSUBISHI PLASTICS IND LTD), 27 January 1998 (1998-01-27) abstract ---	1-21
A	DATABASE WPI Week 9801 Derwent Publications Ltd., London, GB; AN 1998-004290 XP002196361 & JP 09 272789 A (MITSUBISHI CHEM CORP) abstract ---	1-21
A	DATABASE WPI Week 9409 Derwent Publications Ltd., London, GB; AN 1994-071624 XP002196362 & JP 06 024501 A (MITSUI TOATSU CHEM INC) abstract --- -/--	1-21

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

page 2 of 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/00761

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>HIDETO TSUJI ET AL: "BLENDS OF ALIPHATIC POLYESTERS.I. PHYSICAL PROPERTIES AND MORPHOLOGIES OF SOLUTION-CAST BLENDS FROM POLY(DL-LACTIDE) AND POLY(EPILON-CAPROLACTONE)" JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY AND SONS INC. NEW YORK, US, vol. 60, no. 13, 27 June 1996 (1996-06-27), pages 2367-2375, XP000634752 ISSN: 0021-8995 page 2367 table 1 page 2369 -page 2862</p>	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/00761

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9407941	A	14-04-1994	US 5536807 A	16-07-1996
			US 5484881 A	16-01-1996
			US 5338822 A	16-08-1994
			AT 190337 T	15-03-2000
			AU 5295393 A	26-04-1994
			BR 9305660 A	26-11-1996
			CA 2124847 A1	14-04-1994
			DE 69328018 D1	13-04-2000
			DE 69328018 T2	19-10-2000
			EP 0615529 A1	21-09-1994
			ES 2142880 T3	01-05-2000
			FI 942559 A	13-07-1994
			JP 7504227 T	11-05-1995
			NO 942038 A	25-07-1994
			NZ 256972 A	24-04-1997
			US 6093791 A	25-07-2000
			WO 9407941 A1	14-04-1994
			US 6121410 A	19-09-2000
			US 5773562 A	30-06-1998
			US 6005068 A	21-12-1999
			US 6207792 B1	27-03-2001
			US 5585191 A	17-12-1996
			US 5798436 A	25-08-1998
			AT 199944 T	15-04-2001
			AT 173520 T	15-12-1998
			AT 193718 T	15-06-2000
			AU 5294893 A	26-04-1994
			AU 5296393 A	26-04-1994
			AU 660266 B2	15-06-1995
			AU 5350294 A	26-04-1994
			BR 9305657 A	26-11-1996
			BR 9305658 A	26-11-1996
			BR 9305661 A	26-11-1996
			CA 2124846 A1	14-04-1994
			DE 69322155 D1	24-12-1998
			DE 69322155 T2	19-08-1999
			DE 69328822 D1	13-07-2000
			DE 69328822 T2	25-01-2001
			DE 69330046 D1	26-04-2001
			DE 69330046 T2	15-11-2001
			DK 615555 T3	09-07-2001
			DK 615532 T3	16-10-2000
			EP 0615555 A1	21-09-1994
			EP 0624212 A1	17-11-1994
			EP 0615532 A1	21-09-1994
			ES 2156876 T3	01-08-2001
			ES 2123668 T3	16-01-1999
			ES 2149217 T3	01-11-2000
			FI 942558 A	13-07-1994
			FI 942560 A	13-07-1994
US 5866634	A	02-02-1999	JP 9169896 A	30-06-1997
CA 2057668	A	14-06-1993	CA 2057668 A1	14-06-1993
JP 10024518	A	27-01-1998	NONE	
JP 9272789	A	21-10-1997	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/00761

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
JP 6024501	A	01-02-1994	JP	3148367 B2	19-03-2001

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 August 2002 (01.08.2002)

PCT

(10) International Publication Number
WO 02/059201 A1

(51) International Patent Classification⁷: **C08L 67/02**,
67/04

(21) International Application Number: PCT/EP02/00761

(22) International Filing Date: 25 January 2002 (25.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
TO2001A000061 25 January 2001 (25.01.2001) IT

(71) Applicant (for all designated States except US): **NOVA-MONT S.P.A.** [IT/IT]; Via G. Fauser, 8, I-28100 Novara (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BASTIOLI, Ca-**
tia [IT/IT]; Via Della Noce, 63, I-28100 Novara (IT). **DEL TREDICI, Gianfranco** [IT/IT]; Via Sempione, 31,
I-21018 Sesto Calende (IT). **GUANELLA, Italo** [IT/IT];
Via Cavallé 3/A, I-28068 Romentino (IT). **FLORIDI,**
Giovanni [IT/IT]; Via XIII Martiri 8, I-28100 Novara
(IT). **PONTI, Roberto** [IT/IT]; Via Momo, 64, I-28047
Oleggio (IT).

(74) Agents: **RAMBELLI, Paolo** et al.; Jacobacci & Partners
S.p.A., Corso Regio Parco, 27, I-10152 Torino (IT).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW).
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM).
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR). OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted
a patent (Rule 4.17(ii)) for the following designations AE,
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA,
CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES,
FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG,
MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU,
SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG,
UZ, VN, YU, ZA, ZM, ZW; ARIPO patent (GH, GM, KE, LS,
MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW). Eurasian patent
(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). European patent
(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,
MC, NL, PT, SE, TR). OAPI patent (BF, BJ, CF, CG, CI,
CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report

(48) Date of publication of this corrected version:

14 November 2002

(15) Information about Correction:

see PCT Gazette No. 46/2002 of 14 November 2002, Sec-
tion II

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: BINARY MIXTURES OF BIODEGRADABLE ALIPHATIC POLYESTERS AND PRODUCTS OBTAINED FROM THESE

(57) Abstract: A biodegradable mixture obtained by melt mixing polyesters comprising: (A) an aliphatic polyesters of the kind polyhydroxyacid or diacid/diol and their copolymer; (B) a polymer of lactic acid comprising L or D polylactic acid, L, D-polylactic, meso polylactic acid and lactic acid copolymers with hydroxyacids or lactones thereof containing at least 75% of L-lactic or D-lactic acid in which the concentration by weight of A with respect to (A+B) is in the range 30-60% and in which the sum of the fusion enthalpies ΔH_A and ΔH_B of the two polyesters in the mixture is greater than the normalized sum of the fusion enthalpies Δ_1 and Δ_{H_2} of the aliphatic polyesters prior to melt mixing, the fusion enthalpy converted to the polylactic acid-family polymer when the temperature of the film is raised being greater than 35 J/g.

WO 02/059201 A1

THIS PAGE BLANK (USPTO)